Preface

This thesis deals with the non-equilibrium phenomena under shear observed mainly in bilayer forming liquid crystalline phases of mixed surfactant systems, anisotropic colloidal dispersions as well as Langmuir monolayers of membrane peptides. To correlate the structural transitions under shear with the mechanical properties or flow behaviour, the rheological measurements are combined with different techniques such as optical imaging (bright field, polarizing or confocal), small angle light scattering as well as small angle x-ray scattering (Rheo-SAXS) measurements. The bilayer forming phases that have been studied consist of mixed surfactant system formed by a mixture of ionic amphiphiles with strong binding organic counter ions. The propensity of the hydrophobic counterion to modify the spontaneous curvature at the micelle-water interface gives rise to a rich equilibrium phase behaviour consisting of different bilayer forming liquid crystalline mesophases in between the hexagonal and lamellar phases. The liquid crystalline mesophases presently examined under shear are the weakly swollen isotropic and lamellar phases as well as the random and rhombohedral mesh phases. The main motivation of the thesis was to examine the stability of these phases under shear since all the existing studies so far on shear induced structural transitions are mainly confined to highly swollen isotropic sponge phase of interconnecting bilayers that can transform to a lamellar phase consisting of a stack of bilayers with 1D quasi long range order or a dilute lamellar phase is shear transformed to a collapsed surfactant rich lamellar phase coexisting with excess solvent at Peclet Number greater than 1.

The present study revealed for the first time a shear reversible crystallization above the equilibrium crystallization temperature in the weakly swollen isotropic and lamellar phases formed in the SDS-PTHC-water system where the structural transition is feasible through a shear induced segregation/microphase separation of the hydrophobic counterions to tune

the curvature of the bilayer-water interface. These results incited us to examine the role of shear on another class of mesophases that are structurally similar to lamellar phase but with a non-uniform interfacial curvature of the bilayers identified as the intermediate mesh phases. Mesh phases are formed by a 1D stack of perforated bilayers with quasi-long range order where the water filled pores or curvature defects can have a liquid-like ordering in the plane of the bilayers as in a random mesh phase or the pores can have a square or hexagonal ordering locking into a three dimensional lattice with either tetragonal or rhombohedral symmetry to form T_α or R$\bar{3}$m ordered mesh phases. Two characteristic features of the mesh phases that is noteworthy are i) the non-uniform mean curvature for the bilayers formed by 3-coordinated hexagonal mesh or the 4-coordinated square mesh; ii) the elasticity of the bilayers forming the hexagonal or square ordered mesh in R$\bar{3}$m or T_α phases as opposed to the fluid-like bilayers with zero surface shear modulus in the random mesh or classical lamellar phases (L_α). Hence the structural similarity as well as differences of the mesh phases with the lamellar phase raises some pertinent questions regarding the stability of surfactant mesh phases under shear. Two striking consequences of shear flow on the random and ordered mesh phases of a cationic-anionic mixed surfactant system were revealed: a shear-induced 3D ordering of the curvature defects in L_α^D phase as well as a hydrodynamic instability wherein a sequence of structural rearrangements leading to buckling instability gives rise to unstable flows in the R$\bar{3}$m phase. These studies on shear induced structural transitions on partially ordered mesophases is juxtaposed with the study on another class of systems that were examined under shear comprising dispersion of anisotropic colloidal rods. We demonstrate that these suspensions shear thicken at low concentrations ($\geq$ 25 %) and origin of shear thickening is formation of stress bearing hydrodynamic clusters rather than order-disorder transition. Finally we also examine the rheological properties of a monolayer of membrane peptide Alamethicin where the coexistence of solid-like domains in a backround of liquid expanded phase at high surface concetrations gives rise to a dense anisotropic suspension in 2D. The rheological properties of these jammed fluid/fluid interfaces formed by membrane proteins is well explained by the soft glassy rheology model proposed earlier in the context of 3D soft glasses, comprising emulsions, foams, colloidal glasses and gels.

Chapter 1 starts with a general introduction of soft condensed matter systems and then we proceed to describe surfactant systems, their phase behaviour and self assembly. The

formation of liquid crystalline phases in pure surfactant systems and in presence of additives such as salt or counterions are discussed. A brief introduction to colloids is explained further. This is followed by the discussion on the inter-macromolecular forces governing soft matter systems such as van der Waals interaction, the screened Coulomb repulsion, hydrogen bond, depletion, peristaltic, hydrophobic and hydration forces and steric repulsion. We further explain the systems studied and their phase behaviour at different concentrations formed by SDS-PTHC-water, CTAB-SHN-water system in detail. In the next section we describe the characterization of different liquid crystalline phases viz. nematic, hexagonal, isotropic, lamellar, intermediate mesh and ribbon phases using cross polarizing optical microscopy, small angle x-ray and rheology. Then, a theoretical background of linear and nonlinear rheology, optical/confocal microscopy and x-ray scattering techniques are given. This is followed by discussion on flow properties of colloidal suspensions in dilute and semi-dilute regime and finally shear thickening phenomena observed in concentrated suspensions. We discuss shear thickening phenomena observed in anisotropic precipitated calcium carbonate (PCC) colloids. We have also discussed shear induced phase and structural transitions observed in different liquid crystalline phases.

Chapter 2 discusses the experimental apparatus and techniques used in our studies. We have discussed the different components of the MCR-300 and 101 stress-controlled rheometer (Paar Physica, Germany). The cross polarizing optical microscopy in transmission and reflection mode using a home-made shear cell and in built set-up respectively, and small angle light scattering set-up are discussed. Next, we discuss in-situ small angle x-ray rheology setup, a home made Couette cell installed at RRI Bangalore, Couette installed at SWING beamline Soleil, Paris, France and parallel plate setup at PETRA III, Germany. This is followed by discussion on sample preparation and synthesis technique of silica colloidal rods and modification of surface potential using a thermo-responsive polymer. Further, we explain the algorithm to track rods and analysis of SAXS 2D diffraction pattern.

Flow behaviour of different phases formed in SDS-PTHC-water system are described in **Chapter 3**. This chapter has been divided into four sections. In section I, we describe the phase behaviour and rheology of micellar solution at different surfactant concentrations (ϕ) and molar ratios (α = [PTHC]/[SDS]) of two components. At $\phi = 0.3$, a transition from viscous to visco-elastic behaviour is observed with increasing α from 0 to 0.3. Zero

shear viscosity shows a non-monotonic behaviour with increasing α and reveals a maxima at $\alpha = 0.15$. At low α, we observe a Newtonian behaviour which changes to shear thinning behaviour with increasing α and finally again retains the Newtonian behaviour. Dynamic light scattering studies in conjunction with presence of nematic phase made up of disks (confirmed by cross-polarizing optical microscopy) at higher $\alpha > 0.325$, suggest that the drop in zero shear viscosity is due to decrease in length of the micelles from rods to disks. A similar behaviour is observed with increasing ϕ at constant $\alpha = 0.2, 0.25, 0.6$. A change in the morphology of micellar aggregates with increase in α is expected in mixed surfactant systems with strongly binding counterions. However the change in morphology of micellar aggregates with surfactant content in surprising which is witnessed for the first time in mixed surfactant systems.

In section II of this chapter we discuss the phase behaviour and rehological properties of different liquid crystalline phases formed in SDS-PTHC-water system at $\phi = 0.4$, and varying α from 0 to 0.4. Using deutrium nuclear magnetic resonance (NMR) studies we show that the transition from hexagonal phase at $\alpha = 0$, to lamellar phase at $\alpha = 0.4$ occurs through a nemtaic phase of rods at $\alpha = 0.05$ and nemtaic phase of disks at $\alpha = 0.2$ through an isotropic phase of rods at $\alpha = 0.15$. NMR studies reveal a decrease in variation of the quadrupole splitting across the transition from N_C to N_D. The visco-elastic and flow behaviour of the different phases were examined. A decrease in the steady shear viscosity across the different phases with increasing α suggests a decrease in the aspect ratio of the micellar aggregates. From the transient shear stress response of the N_C and N_D nematic phases in step shear experiments, they were characterized to be tumbling and flow aligning, respectively. Our studies reveal that by tuning the morphology of the surfactant micelles, strongly binding counterions modify the phase behaviour and rheological properties of concentrated surfactant solutions.

In section III, we discuss shear induced phase transition in SDS-PTHC-water system using in-situ rheo-optical imaging and in-situ rheo-SAXS. Bilayer forming liquid crystalline phases namely isotropic (L_i - optically isotropic) and lamellar (L_α - optically birefringence) are formed at $\alpha = 1.5$, $\phi = 0.4$ and $\alpha = 1$, $\phi = 0.5$. Both phases co-exist with excess solvent and remain fully swollen at temperature $T > 50\ ^oC$. We have constructed a dynamic phase diagram in the parameter space of shear rate and temperature which demonstrate a

novel shear induced phase transition to a crystalline phase (L_c) above a critical shear rate. At constant shear rate, the increase in viscosity is accompanied by presence of birefringent texture of L_α phase after a waiting time (t) which decreases with increasing shear rate. The L_c phase is stable under shear and melts back to equilibrium L_i phase once shear is stopped. At higher temperature a transition from $L_i \rightarrow L_\alpha$ is observed. In-situ small angle x-ray scattering reveals an evolution of additional peaks in small as well as wide angle region which does not evolve any further once the viscosity reaches a maxima. The L_c phase obtained under shear at different shear rates can be indexed to a triclinic lattice with the lattice parameters depending on shear rates. We propose that the possible origin of phase transition is re-distribution of counterions under shear which results in counterion-rich and counterion-poor region. This counterion rich region results in crystalline L_c phase. In addition to revealing a unique class of non-equilibrium phase transition, the present study urges a unique approach toward understanding shear-induced phenomena in concentrated meso-phases of mixed amphiphilic systems

In section IV we propose a shear induced nucleation and growth of crystalline phase in metastable bilayer forming L_i and L_α phases. Nucleation and growth of crystalline phase accelerated by shear exhibits a power law dependence on time. The time of nucleation strongly depends on the shear rate with different exponents for different phase compositions. The crystalline phase formed under the influence of shear is stable and irreversible for temperature $< 28\ ^oC$. The crystal structure obtained under shear can be indexed to a triclinic unit cell with different lattice parameters depending on the shear rate and concentration probed.

In **Chapter 4**, we discuss shear induced transitions observed in mesh phases formed in cationic surfactant system CTAB in the presence of strongly binding counterions SHN formed at different surfactant concentration (ϕ) and molar ratio (α). Random mesh phase (L_α^D) formed at $\phi = 0.3$, 0.4, 0.5 and $\alpha = 1$ are identified as stack of bilayers having curvature defects in form of water filled pores in the plane of bilayers . These pores do not have any long range correlation either in-plane or across the plane. A 3D ordered mesh phase ($R\bar{3}m$) is formed at $\alpha = 1$ and $\phi = 0.6$, where these pores have in-plane and out of plane positional correlation and locked into a 3D lattice with rhombohedral symmetry. These phases are easily identified from small angle x-ray scattering studies wherein L_α^D a diffuse peak corresponding to in-plane defect spacing (d_{def}) is observed along with lamellar d-spacing (d). However

several additional peaks along with lamellar peak are observed for R$\bar{3}$m phase revealing a long range correlation of pores. By shearing different L_α^D phases formed at different ϕ's, we probe the effect of shear far and near to the R$\bar{3}$m phase boundary. When L_α^D phases formed at $\phi = 0.3$ and 0.4 are sheared at constant shear rate, we observe a structural transition to an onion phase which is accompanied by increase in viscosity at the onset of the transition. When L_α^D phase formed near R$\bar{3}$m phase at $\phi = 0.5$ is sheared, we observe a decrease in viscosity which is accompanied by the presence of a sharp peak near the diffuse peak corresponding to d_{def} along with several other small as well as wide angle peaks. All these peaks can be indexed to R$\bar{3}$m phase co-existing with equilibrium L_α^D phase. We propose that the locking of the defects into a 3D lattice occurs when the in-plane correlation length (d_{def}) is larger than the bilayer periodicity (d). Prior to appearance of sharp peak near d_{def}, we observe an a-orientation of lamellae i.e. bilayers align along the shear-gradient plane where shear is likely to increase the length of cylindrical arrays or rods. A shear driven increase in the length of the rods implies a larger radius of this in-plane circle forming the pores, leading to a lower curvature and consequently a lower curvature energy. This increase in average size of the pores under shear favored by the lower curvature energy is expected to increase the in-plane as well as the trans-bilayer correlation length of the defects. The $L_\alpha \rightarrow$ R$\bar{3}$m phase transition is also observed in another system cetylpyridinium chloride (CPCl)-SHN-water. Thus this type of transition is general feature of random mesh phases when sheared near R$\bar{3}$m phase in the equilibrium phase diagram. A thixotropic behaviour with yield stress (σ_y) = 500 Pa, is observed when equilibrium R$\bar{3}$m phase is sheared. When the shear stress crosses a threshold value of 1000 Pa, we observe an avalanche behaviour with drop in viscosity of more than 4 orders of magnitude. This drop is accompanied by appearance of several sharp peaks which can be indexed to two or three R$\bar{3}$m phases. The similar transition is observed under shear in R$\bar{3}$m phase formed in CPCl-SHN-water system. We propose that shearing a 3D ordered lattice of defects as in the R$\bar{3}$m phase leads to additional structural transitions, though the rhombohedral symmentry is retained.

In **Chapter 5**, we discuss shear thickening observed in colloidal rods. Using rheology combined with microscopy, we demonstrate that origin of shear thickening in colloidal rods is the formation of hydroclusters and not order-disorder transition. We observe continuous

(CST) as well as discontinuous shear thickening (DST) at volume fractions of colloidal suspension at 25 % and $>$ 30 % respectively. In DST, in controlled stress measurements, flow curve exhibits an S-shaped flow curve (stress vs. shear rate) where we observe a negative slope in shear thickening regime. By combining fast confocal microscopy with rheometer (parallel plate geometry), we investigate the possible mechanism for shear thickening in our suspension and rule out order-disorder transition. This indicates that the shear thickening might be a consequence of formation of hydroclusters which is confirmed by modifying surface properties of these colloids where a thermo responsive microgel PNIPAM was used as a shell to the silica core. The advantage of using PNIPAM is that the polymer brush remains fully swollen below the lower critical solution temperature (LCST) and shrinks above the LCST (34 ^{o}C) acting as hard particles. Thus by controlling the temperature, the interparticle separation can be tuned. We observe a pure shear thinning and shear thickening behaviour below and above LCST respectively. We show that by changing the interparticle separation we can avoid hydrocluster formation arsing due to the hydrodynamic lubrication forces responsible for the shear thickening. The calculation the order parameter and measurements on core-shell particles illustrate that microscopic origin of shear thickening is the formation of hydroclusters and not order-disorder transition.

Chapter 6 deals with the 2D interfacial rheology of antibiotic alamethecin film at air-water interface. Fluorescence microscopy of alamethicin monolayers revealed a coexistence of liquid expanded (LE) and solid phases at the surface concentrations studied. Interfacial oscillatory shear measurements on alamethicin monolayers indicate that its viscoelastic properties are determined by the area fraction of the solid domains. The role of zwitterionic phospholipids dioleoylphosphatidyl choline (DOPC) and dioleoylphosphatidyl ethanolamine (DOPE) on the peptide aggregation behaviour was investigated. Fluorescence microscopy of alamethicin/phospholipid monolayers revealed an intermediate phase (I) in addition to the solid and LE phase. In mixed monolayers of phospholipid (L)/alamethicin (P), with increase in L/P, the monolayer transforms from a viscoelastic to a viscous fluid with the increase in area fraction of the intermediate phase. Further, a homogeneous mixing of alamethicin/lipid molecules is observed at L/P$>$4. Our studies also confirm that the visco-elasticity of alamethicin/phospholipid monolayers is closely related to the alamethicin/phospholipid interactions at the air-water interface.